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Phase-field Model for Stress-dependent Ginsburg-Landau Kinetics for Large Deformation of Silicon Anodes

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Disclaimer

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Title: Phase-field model for stress-dependent Ginsburg-Landau kinetics for large deformation of silicon anodes

Personnel: Dr. Yonghao An, postdoctoral fellow under the supervision of Prof. Hanqing Jiang

Purpose: Provide phase-field model for large deformation of silicon anodes for Li-ion batteries based on stress-dependent Ginsberg-Landau kinetics

Period of work: 4/2014 to 6/2014

Work locations: Arizona State University

Project description:

Silicon is considered as one of the most promising anode materials for next generation of Lithium ion batteries, due to its high theoretical capacity. Experiments have confirmed the initial lithiation of crystal silicon during discharging of batteries always involve huge volume expansion[1], plastic flow of material[2], phase transformation from crystal to amorphous[3], and mass diffusion of lithium ions[4], which in together govern the performance of this electrode materials. Despite progresses in continuum mechanics modeling[5] and atomic calculations[6] to address this problem, a phase field modeling has its own advantages, especially to capture the widely observed sharp phase boundary, and electrochemically driven anisotropic amorphization. Under the subcontract, a phase field model is rigorously developed under the framework of large deformation. Spedifically, the stress-dependent Ginsberg-Landau equation is derived for the first time in large deformation, which could be used to discuss the coupling effect of phase transformation/deformation and implications to experiments and future battery designs [7, 8].

Summary of results:

Eight field variables are introduced to fully describe the status of the material, including elastic stretches λ_i^e ($i=1,2,3$), plastic stretches λ_i^p ($i=1,2,3$, only two of them are independent because the incompressibility of plastic deformation as $\lambda_1^p\lambda_2^p\lambda_3^p=1$), Li content c ($0\le c\le 1$), and crystallinity η ($0\le\eta\le 1$, with $\eta=0,1$ denoting amorphous and crystal phases). The volume expansion induced by lithiation is assumed linearly dependent on Li content, as $v^c=\lambda_1^e\lambda_2^e\lambda_3^e=1+\beta c$. It is also assumed that crystallinity is determined by Li content as $\eta=1-c$, given the observation that crystal/amorphous phases are always associated with low/high Li content. Therefore, five independent variables are in need.

Total free energy of the system reads $F_{tot}=\int_V F dV$, with dV and F are the volume element and energy density in original configuration. The free energy of the system is considered to have contributions from three parts, $F=F_{el}+F_{ch}+\frac{\theta^2}{2}(\nabla\eta)^2$. Here F_{el}, and F_{ch}, are the nominal density of elastic energy and chemical energy in volume. $\frac{\theta^2}{2}(\nabla\eta)^2$ is energy arising from gradient of crystallinity at interface between two phases. ∇ is the gradient operator in original configuration. The coefficient θ is assumed constant. The thermodynamic forces conjugated to state variables are

derived by variation of free energy and thermodynamic inequality, as $\sigma_i = \frac{1}{\lambda_1^e \lambda_2^e \lambda_3^e} \frac{\partial F}{\partial \ln \lambda_i^e}$, and $\Gamma = \frac{1}{\lambda_1^e \lambda_2^e \lambda_3^e}\left(\frac{\partial F}{\partial \eta} - \theta^2 \nabla^2 \eta\right) - \frac{\beta \sigma_h}{1+\beta\eta}$. Here σ_i is the principle value of Cauchy stress σ_{ij}, λ_i is the total stretch, and σ_h is the hydrostatic part of σ_{ij}. To give the governing equations for the coupled deformation and phase change problem, the stress is assumed balanced implying the mechanical equilibrium for deformation, as in $\partial \sigma_{ij} / \partial x_i = 0$, while the "phase force" Γ is unbalanced, giving rise to the Ginsburg–Landau kinetics for phase change, as in $\partial \eta / \partial t = -m\Gamma$. Here x_i is the current position, m is the interface mobility of the interface. As we can see, hydrostatic stress and deformation enter the Ginsburg–Landau kinetics through the definition of Γ in this coupling problem.

Fig. 1 shows the color map of phases and maximum stress on the deformed cross section of Si nanowires. The anisotropic interface mobility is considered, while the stress and deformation dependence is turned off in kinetics. It is shown that faceted crystal cores are formed with high level of stress concentrated at the sharp corners. This high level of stress is expected to resist the local interface migration, and effectively round off the sharp corners, when the stress dependent Ginsburg–Landau kinetics is considered.

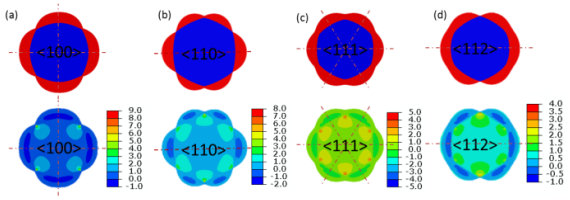

Fig. 1. Color map of phases (amorphous in red, crystal in blue) and maximum in-plane stress (in GPa) on the deformed cross section of (a) <100>; (b) <110>; (c) <111>; (d) <112> crystal silicon nanowires after partially lithiated.

Through the work performed under this subcontract, the theoretical framework for stress dependent Ginsberg-Landau kinetics is established. For the future work, detailed form of chemical energy and material parameters such as θ and m have to be constructed, possibly making use of our computational capability at atomic scale.

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